

WEST Search History

DATE: Monday, August 04, 2003

<u>Set Name</u>	<u>Query</u>	<u>Hit Count</u>	<u>Set Name</u>
side by side			result set
<i>DB=USPT,PGPB,JPAB,EPAB,DWPI; THES=ASSIGNEE; PLUR=YES; OP=ADJ</i>			
L11	L10 and diesel fuel and jet fuel	4	L11
L10	L9 and petroleum	13	L10
L9	L8 and (blend\$3 or combin\$3)	13	L9
L8	L7 and extraction	13	L8
L7	L6 and distillation	16	L7
L6	L5 and adsorbent	21	L6
L5	L4 and hydrotreat\$3	59	L5
L4	L3 and alcohol	96	L4
L3	L2 and (measure oxygenat\$2 or remov\$3 near2 oxygenat\$2)	115	L3
L2	L1 and (oxygenated species or oxygenated compound or oxygenates)	729	L2
L1	fischer near1 tropsch	5572	L1

END OF SEARCH HISTORY

[Generate Collection](#)[Print](#)**Search Results - Record(s) 1 through 9 of 9 returned.** 1. Document ID: US 20020128530 A1

L12: Entry 1 of 9

File: PGPB

Sep 12, 2002

PGPUB-DOCUMENT-NUMBER: 20020128530

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20020128530 A1

TITLE: Dimerizing olefins to make lube base stocks

PUBLICATION-DATE: September 12, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Miller, Stephen J.	San Francisco	CA	US	
Krug, Russell R.	Novato	CA	US	

APPL-NO: 09/ 758670 [PALM]

DATE FILED: January 11, 2001

INT-CL: [07] C07 C 2/04, C07 C 2/08

US-CL-PUBLISHED: 585/517; 585/510, 585/518, 585/329, 585/324

US-CL-CURRENT: 585/517; 585/324, 585/329, 585/510, 585/518

REPRESENTATIVE-FIGURES: NONE

ABSTRACT:

Lube base stock compositions, and methods for preparing the compositions, are disclosed. The methods involve subjecting a predominantly C.sub.5-11 olefin-containing feedstock to dimerization conditions, preferably using nickel ZSM-5 as the dimerization catalyst, to give a first product where the majority of the olefins in the olefinic feed are converted to hydrocarbons predominantly in the C.sub.10-22 range. The first product, optionally combined with an olefin-containing feed in the C.sub.10-22 range, preferably in the C.sub.12-18 range, is subjected to an additional dimerization step, using the same or a similar dimerization catalyst, to provide a second product that includes hydrocarbons in the lube base stock range. The olefinic feedstock may include paraffins as well as olefins, which paraffins do not participate in the dimerization reactions. Accordingly, the second product includes relatively heavy hydrocarbons in the lube base stock range, as well as the relatively light unreacted paraffins (and any unreacted olefins). The hydrocarbons in the lube base stock range can be readily separated, for example, via distillation. In one embodiment, at least a portion of the olefin-containing feeds is derived, in whole or in part, from Fischer-Tropsch synthesis.

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KMC
Draw	Desc	Image									

 2. Document ID: US 20020115732 A1

PGPUB-DOCUMENT-NUMBER: 20020115732
 PGPUB-FILING-TYPE: new
 DOCUMENT-IDENTIFIER: US 20020115732 A1

TITLE: Removing sulfur from hydroprocessed fischer-tropsch products

PUBLICATION-DATE: August 22, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Moore, Richard O. JR.	San Rafael	CA	US	
Gelder, Roger D. Van	Beaconsfield		GB	
Hilton, Grant C.	Woking		GB	
Jones, Clive	Reading		GB	

APPL-NO: 09/ 789143 [PALM]
 DATE FILED: February 20, 2001

INT-CL: [07] C07 C 27/06

US-CL-PUBLISHED: 518/705; 208/178
 US-CL-CURRENT: 518/705; 208/178

REPRESENTATIVE-FIGURES: 1

ABSTRACT:

An integrated process for producing desulfurized hydroprocessed products from Fischer-Tropsch synthesis is disclosed. The process involves isolating and desulfurizing a methane-rich stream from a natural gas source in a first separation zone and a desulfurization zone. The methane-rich stream is converted to syngas and subjected to a hydrocarbon synthesis step, for example, a Fischer-Tropsch synthesis step. The products from the hydrocarbon synthesis step typically include a C._{sub.4}- fraction, a C._{sub.5-20} fraction, and a C._{sub.20+} wax fraction. These fractions are isolated in a second separation zone, typically via fractional distillation. The C._{sub.4}- fraction can be recycled through the first separation zone to provide a second methane-rich fraction for conversion to synthesis gas. The C._{sub.4}- fraction can optionally be treated, for example, with hydrotreatment or hydroisomerization catalysts and conditions before or after passage through the first separation zone. The hydrocarbons in the C._{sub.5-20} and C._{sub.20+} wax fractions are subjected to additional process steps, for example, hydrotreatment, hydroisomerization, hydrocracking (particularly in the case of the wax fraction), preferably in the presence of sulfurcontaining compounds. The products of the additional process steps are sent to a third separation zone, and yield one or more fractions useful, for example, in fuel-related products (preferably C._{sub.5-20} hydrocarbons) as well as an additional C_{sub.4}- fraction. The additional C_{sub.4}- fraction, which can include sulfur impurities resulting from the hydroconversion reaction, can also be desulfurized in the desulfurization zone along with the natural gas. This eliminates the need for a second desulfurization zone. The desulfurization zone can be scaled up from its normal size, if desired, to accommodate the additional sulfur removal resulting from the hydroconversion.

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KMC
Draw Desc	Image										

3. Document ID: US 20020003102 A1

PGPUB-DOCUMENT-NUMBER: 20020003102
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020003102 A1

TITLE: Process for making a lube base stockfrom a lower molecular weight feedstock
PUBLICATION-DATE: January 10, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
O'Rear, Dennis J.	Petaluma	CA	US	
Harris, Thomas V.	Benicia	CA	US	
Miller, Stephen J.	San Francisco	CA	US	
Krug, Russell R.	Novato	CA	US	
Lok, Brent K.	San Francisco	CA	US	

APPL-NO: 09/ 758813 [PALM]
DATE FILED: January 11, 2001

RELATED-US-APPL-DATA:

Application 09/758813 is a continuation-in-part-of US application 09/470053, filed December 22, 1999, PENDING

INT-CL: [07] C10 G 71/00, C10 G 57/02

US-CL-PUBLISHED: 208/18; 208/49, 208/62, 208/74
US-CL-CURRENT: 208/18; 208/49, 208/62, 208/74

REPRESENTATIVE-FIGURES: NONE

ABSTRACT:

A process for making a lube base stock wherein a highly paraffinic feedstock is dehydrogenated to produce an olefinic feedstock. That olefinic feedstock is contacted with an oligomerization catalyst in an oligomerization zone to produce a product having a higher number average molecular weight than the olefinic feedstock. The product is separated into a light byproduct fraction and a heavy product fraction. The heavy product fraction comprises a lube base stock.

[0001] This application is a continuation-in-part of U.S. Ser. No. 09/470,053, filed Dec. 21, 1999, titled "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock," and is also related to two applications filed concurrently with this application, with the titles "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock Using At Least Two Oligomerization Zones" and "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock In A Catalytic Distillation Unit."

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw	Desc	Image							KMC

4. Document ID: US 20010006154 A1

L12: Entry 4 of 9

File: PGPB

Jul 5, 2001

PGPUB-DOCUMENT-NUMBER: 20010006154
PGPUB-FILING-TYPE: new-utility
DOCUMENT-IDENTIFIER: US 20010006154 A1

TITLE: Process for making a lube base stockfrom a lower molecular weight feedstockin a catalytic distillation unit

PUBLICATION-DATE: July 5, 2001

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Krug, Russell R.	Novato	CA	US	
O'Rear, Dennis J.	Petaluma	CA	US	

APPL-NO: 09/ 758667 [PALM]
DATE FILED: January 11, 2001

RELATED-US-APPL-DATA:

Application 09/758667 is a continuation-in-part-of US application 09/470053, filed December 22, 1999, PENDING

INT-CL: [07] C10 G 71/00, C07 C 2/12, C07 C 2/10, C07 C 2/02

US-CL-PUBLISHED: 208/18; 585/502, 585/504, 585/531, 203/29, 203/DIG.006
US-CL-CURRENT: 208/18; 203/29, 203/DIG.6, 585/502, 585/504, 585/531

REPRESENTATIVE-FIGURES: NONE

ABSTRACT:

A process for making a lube base stock wherein an olefinic feedstock is contacted with an oligomerization catalyst in a catalytic distillation unit to produce a product having a higher number average molecular weight than the olefinic feedstock. That product is separated zone in the catalytic distillation unit into a light byproduct fraction and a heavy product fraction that includes hydrocarbons in a lube base stock range.

RELATED APPLICATIONS

[0001] This application is related to "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock," filed concurrently with this application, which is a continuation-in-part of U.S. Ser. No. 09/470,053, titled "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock," filed Dec. 21, 1999. This application is also related to "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock Using At Least Two Oligomerization Zones," filed concurrently with this application.

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								KMC

5. Document ID: US 20010004972 A1

L12: Entry 5 of 9

File: PGPB

Jun 28, 2001

PGPUB-DOCUMENT-NUMBER: 20010004972
PGPUB-FILING-TYPE: new-utility
DOCUMENT-IDENTIFIER: US 20010004972 A1

TITLE: Process for making a lube base stock from a lower molecular weight feedstock using at least two oligomerization zones

PUBLICATION-DATE: June 28, 2001

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Miller, Stephen J.	San Francisco	CA	US	
O'Rear, Dennis J.	Petaluma	CA	US	
Harris, Thomas V.	Benicia	CA	US	
Krug, Russell R.	Novato	CA	US	

APPL-NO: 09/ 758897 [PALM]
 DATE FILED: January 11, 2001

RELATED-US-APPL-DATA:

Application 09/758897 is a continuation-in-part-of US application 09/470053, filed December 22, 1999, PENDING

INT-CL: [07] C10 G 71/00

US-CL-PUBLISHED: 208/18; 208/19, 585/302, 585/304, 585/314, 585/326, 585/502, 585/531

US-CL-CURRENT: 208/18; 208/19, 585/302, 585/304, 585/314, 585/326, 585/502, 585/531

REPRESENTATIVE-FIGURES: NONE

ABSTRACT:

A process for making a lube base stock wherein an olefinic feedstock is separated into a light olefin fraction and a medium olefin fraction. The light olefin fraction is contacted with a first oligomerization catalyst in a first oligomerization zone to produce a first product. Both the medium olefin fraction and the first product are contacted with a second oligomerization catalyst in a second oligomerization zone to produce a second product. The second product is separated into a light byproduct fraction and a heavy product fraction that includes hydrocarbons in the lube base stock range.

RELATED APPLICATIONS

[0001] This application is related to "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock," filed concurrently with this application, which is a continuation-in-part of U.S. Ser. No. 09/470,053, titled "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock," filed Dec. 21, 1999. This application is also related to "A Process For Making A Lube Base Stock From A Lower Molecular Weight Feedstock In A Catalytic Distillation Unit," filed concurrently with this application, and to "Use of a Hydrogen-containing Gas Stream to Retard Fouling of Preheat Exchangers in Fischer-Tropsch Products Hydroprocessing," also filed concurrently with this application.

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWIC

6. Document ID: US 6566411 B2

L12: Entry 6 of 9

File: USPT

May 20, 2003

US-PAT-NO: 6566411

DOCUMENT-IDENTIFIER: US 6566411 B2

TITLE: Removing sulfur from hydroprocessed fischer-tropsch products

DATE-ISSUED: May 20, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Moore, Jr.; Richard O.	San Rafael	CA		
Van Gelder; Roger D.	Beaconsfield			GB
Hilton; Grant C.	Woking			GB
Jones; Clive	Reading			GB

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
Chevron U.S.A. Inc.	San Ramon	CA			02

APPL-NO: 09/ 789143 [PALM]
 DATE FILED: February 20, 2001

INT-CL: [07] C07 C 27/00, C10 G 47/00, C10 G 15/00, C10 G 35/06, C10 G 45/00

US-CL-ISSUED: 518/700; 518/702, 218/58, 218/106, 218/137, 218/142, 218/208R
 US-CL-CURRENT: 518/700; 208/208R, 218/106, 218/137, 218/142, 218/58, 518/702

FIELD-OF-SEARCH: 518/700, 518/702, 208/58, 208/106, 208/137, 208/142, 208/28R

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3852207</u>	December 1974	Strangeland et al.	
<u>3904513</u>	September 1975	Fischer et al.	
<u>4157294</u>	June 1979	Iwao et al.	
<u>4347121</u>	August 1982	Mayer et al.	
<u>4401556</u>	August 1983	Bezman et al.	
<u>4568663</u>	February 1986	Mauldin	
<u>4810357</u>	March 1989	Chester et al.	
<u>4820402</u>	April 1989	Partridge et al.	
<u>4913799</u>	April 1990	Gortsema et al.	
<u>5059567</u>	October 1991	Linsten et al.	
<u>5073530</u>	December 1991	Bezman et al.	
<u>5114563</u>	May 1992	Lok et al.	
<u>5162282</u>	November 1992	Lopez et al.	
<u>5198203</u>	March 1993	Kresge et al.	
<u>5246689</u>	September 1993	Beck et al.	
<u>5334368</u>	August 1994	Beck et al.	
<u>5750819</u>	May 1998	Wittenbrink et al.	
<u>5852061</u>	December 1998	Alexion et al.	
<u>5960643</u>	October 1999	Kuechler et al.	
<u>6075061</u>	June 2000	Wittenbrink et al.	
<u>6147126</u>	November 2000	DeGeorge et al.	

FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0609079	August 1994	EP	
2178756	February 1987	GB	
59176388	October 1984	JP	
99/13963	March 1999	WO	
99/37736	July 1999	WO	
99/37741	July 1999	WO	
00/00571	January 2000	WO	

OTHER PUBLICATIONS

Beck, J., et al., "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates", J. Am. Chem. Soc., 114: 10834-10843 (1992) American Chemical Society, Washington, D.C.

Kresge, C., et al., "Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism", Nature, 359: 710 (1992).

ART-UNIT: 1621

PRIMARY-EXAMINER: Parsa; J.

ATTY-AGENT-FIRM: Burns, Doane, Swecker & Mathis, L.L.P.

ABSTRACT:

An integrated process for producing desulfurized hydroprocessed products from Fischer-Tropsch synthesis is disclosed. The process involves isolating and desulfurizing a methane-rich stream from a natural gas source in a first separation zone and a desulfurization zone. The methane-rich stream is converted to syngas and subjected to a hydrocarbon synthesis step, for example, a Fischer-Tropsch synthesis step. The products from the hydrocarbon synthesis step typically include a C._{sub.4} - fraction, a C._{sub.5-20} fraction, and a C._{sub.20} + wax fraction. These fractions are isolated in a second separation zone, typically via fractional distillation. The C._{sub.4} - fraction can be recycled through the first separation zone to provide a second methane-rich fraction for conversion to synthesis gas. The C._{sub.4} - fraction can optionally be treated, for example, with hydrotreatment or hydroisomerization catalysts and conditions before or after passage through the first separation zone. The hydrocarbons in the C._{sub.5-20} and C._{sub.20} + wax fractions are subjected to additional process steps, for example, hydrotreatment, hydroisomerization, hydrocracking (particularly in the case of the wax fraction), preferably in the presence of sulfur-containing compounds. The products of the additional process steps are sent to a third separation zone, and yield one or more fractions useful, for example, in fuel-related products (preferably C._{sub.5-20} hydrocarbons) as well as an additional C₄- fraction. The additional C₄- fraction, which can include sulfur impurities resulting from the hydroconversion reaction, can also be desulfurized in the desulfurization zone along with the natural gas. This eliminates the need for a second desulfurization zone. The desulfurization zone can be scaled up from its normal size, if desired, to accommodate the additional sulfur removal resulting from the hydroconversion.

12 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
									KMC

7. Document ID: US 6518473 B2

L12: Entry 7 of 9

File: USPT

Feb 11, 2003

US-PAT-NO: 6518473

DOCUMENT-IDENTIFIER: US 6518473 B2

TITLE: Dimerizing olefins to make lube base stocks

DATE-ISSUED: February 11, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Miller; Stephen J.	San Francisco	CA		
Krug; Russell R.	Novato	CA		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
Chevron U.S.A. Inc.	San Ramon	CA			02

APPL-NO: 09/ 758670 [PALM]

DATE FILED: January 11, 2001

INT-CL: [07] C07 C 2/02

US-CL-ISSUED: 585/517; 585/510, 585/518, 585/327, 585/324

US-CL-CURRENT: 585/517; 585/324, 585/327, 585/510, 585/518

FIELD-OF-SEARCH: 585/517, 585/510, 585/518, 585/327, 585/324

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3852207</u>	December 1974	Stangeland et al.	208/58
<u>3904513</u>	September 1975	Fischer et al.	208/18
<u>4053534</u>	October 1977	Mitchell et al.	260/583
<u>4157294</u>	June 1979	Iwao et al.	208/264
<u>4401556</u>	August 1983	Bezman et al.	208/111
<u>4417088</u>	November 1983	Miller	585/530
<u>4482752</u>	November 1984	Mitchell et al.	585/670
<u>4513156</u>	April 1985	Tabak	585/324
<u>4523045</u>	June 1985	Vora	585/254
<u>4523048</u>	June 1985	Vora	585/323
<u>4551438</u>	November 1985	Miller	502/62
<u>4608450</u>	August 1986	Miller	585/517
<u>4657661</u>	April 1987	Miller	208/58
<u>4820402</u>	April 1989	Partridge et al.	208/111
<u>4913799</u>	April 1990	Gortsema et al.	208/89
<u>5012021</u>	April 1991	Vora et al.	585/315
<u>5059567</u>	October 1991	Linsten et al.	502/64
<u>5073530</u>	December 1991	Bezman et al.	502/65
<u>5082986</u>	January 1992	Miller	585/667
<u>5105049</u>	April 1992	Hasselbring	585/516
<u>5114563</u>	May 1992	Lok et al.	208/114
<u>5118902</u>	June 1992	Drake	585/516
<u>5135638</u>	August 1992	Miller	208/27
<u>5198203</u>	March 1993	Kresge et al.	423/718
<u>5198597</u>	March 1993	O'Young et al.	585/654
<u>5246566</u>	September 1993	Miller	208/27
<u>5246689</u>	September 1993	Beck et al.	423/705
<u>5282958</u>	February 1994	Santilli et al.	208/111
<u>5334368</u>	August 1994	Beck et al.	423/704

<u>5334368</u>	August 1994	Beck et al.	423/704
<u>5413695</u>	May 1995	Miller	208/28
<u>5502018</u>	March 1996	Chauvin et al.	502/152
<u>5741759</u>	April 1998	Gee et al.	507/103
<u>5866746</u>	February 1999	Didillion et al.	585/661
<u>5965783</u>	October 1999	Gee et al.	585/664
<u>6004256</u>	December 1999	Townsend et al.	508/503

OTHER PUBLICATIONS

Dornte, R. W., Oxidation of White Oils, Industrial and Engineering Chemistry, Industrial Edition, Jan., 1936, vol. 28, No. 1, Published by American Chemical Society, Easton, PA. pp. 26-30.

ART-UNIT: 1764

PRIMARY-EXAMINER: Dang; Thuan D.

ATTY-AGENT-FIRM: Burns, Doane, Swecker & Mathis, L.L.P.

ABSTRACT:

Lube base stock compositions, and methods for preparing the compositions, are disclosed. The methods involve subjecting a predominantly C._{sub.5-11} olefin-containing feedstock to dimerization conditions, preferably using nickel ZSM-5 as the dimerization catalyst, to give a first product where the majority of the olefins in the olefinic feed are converted to hydrocarbons predominantly in the C._{sub.10-22} range. The first product, optionally combined with an olefin-containing feed in the C._{sub.10-22} range, preferably in the C._{sub.12-18} range, is subjected to an additional dimerization step, using the same or a similar dimerization catalyst, to provide a second product that includes hydrocarbons in the lube base stock range. The olefinic feedstock may include paraffins as well as olefins, which paraffins do not participate in the dimerization reactions. Accordingly, the second product includes relatively heavy hydrocarbons in the lube base stock range, as well as the relatively light unreacted paraffins (and any unreacted olefins). The hydrocarbons in the lube base stock range can be readily separated, for example, via distillation. In one embodiment, at least a portion of the olefin-containing feeds is derived, in whole or in part, from Fischer-Tropsch synthesis.

22 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWIC
Draw Desc	Image									

8. Document ID: US 4973790 A

L12: Entry 8 of 9

File: USPT

Nov 27, 1990

US-PAT-NO: 4973790

DOCUMENT-IDENTIFIER: US 4973790 A

TITLE: Process for upgrading light olefinic streams

DATE-ISSUED: November 27, 1990

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Beech, Jr.; James H.	Wilmington	DE		
Ragonese; Francis P.	Cherry Hill	NJ		
Stoos; James A.	Blackwood	NJ		
Yurchak; Sergei	Media	PA		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
Mobil Oil Corporation	New York	NY			02

APPL-NO: 07/ 437138 [PALM]
DATE FILED: November 16, 1989

INT-CL: [05] C07C 2/02, C07C 2/04

US-CL-ISSUED: 585/533; 585/330, 585/518, 208/70
US-CL-CURRENT: 585/533; 208/70, 585/330, 585/518

FIELD-OF-SEARCH: 585/533, 585/330, 585/518, 208/70

PRIOR-ART-DISCLOSED:**U.S. PATENT DOCUMENTS**

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>2558137</u>	June 1951	Hepp	583/518
<u>2775637</u>	December 1956	Lanning et al.	585/518
<u>3432573</u>	March 1969	Keil	585/518
<u>3960978</u>	June 1976	Coiven et al.	585/533
<u>4070411</u>	January 1978	Butter et al.	585/533
<u>4117087</u>	November 1983	Miller	585/533
<u>4513156</u>	April 1985	Tabak	585/517
<u>4542251</u>	September 1985	Miller	585/533
<u>4544792</u>	October 1985	Smith et al.	585/533
<u>4554396</u>	November 1985	Chang et al.	585/533
<u>4675460</u>	June 1987	Seddon et al.	585/533
<u>4754096</u>	June 1988	Chang et al.	585/533
<u>4777316</u>	October 1988	Harandi et al.	585/517
<u>4855524</u>	August 1989	Harandi et al.	585/533
<u>4865718</u>	September 1989	Herbst et al.	585/530

ART-UNIT: 116

PRIMARY-EXAMINER: Myers; Helane E.

ATTY-AGENT-FIRM: McKillop; Alexander J. Speciale; Charles J. Stone; Richard D.

ABSTRACT:

A process for oligomerizing C2 to C10 olefins obtained by catalytic cracking of heavy crude oil is disclosed. The olefins are oligomerized in the presence of added hydrogen over a shape selective zeolite to gasoline and distillate products. Feed pretreatment, to remove basic nitrogen compounds present in light olefin stream in refinery, with water wash or a guard bed is practiced improves catalyst life.

15 Claims, 3 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWC

9. Document ID: US 4111792 A

L12: Entry 9 of 9

File: USPT

Sep 5, 1978

US-PAT-NO: 4111792
DOCUMENT-IDENTIFIER: US 4111792 A
** See image for Certificate of Correction **

TITLE: Combination process for upgrading synthol naphtha fractions

DATE-ISSUED: September 5, 1978

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Caesar; Philip D.	Princeton	NJ		
Garwood; William E.	Haddonfield	NJ		
Krudewig; William F.	Riverton	NJ		
Wise; John J.	Media	PA		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
Mobil Oil Corporation	New York	NY			02

APPL-NO: 05/ 767876 [PALM]
DATE FILED: February 11, 1977

PARENT-CASE:

RELATED APPLICATION This application is a continuation-in-part of Ser. No. 732,235 filed Oct. 14, 1976.

INT-CL: [02] C07C 15/02, C10G 37/02

US-CL-ISSUED: 208/79; 208/57, 260/673, 260/673.5
US-CL-CURRENT: 208/79; 208/57, 208/950, 518/703, 518/705, 518/728, 585/251, 585/277,
585/407

FIELD-OF-SEARCH: 208/79, 208/80, 208/57, 208/62

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3928174</u>	December 1975	Bonacci et al.	208/80
<u>3965205</u>	June 1976	Garwood et al.	208/120 X
<u>4041094</u>	August 1977	Kuo et al.	208/79 X
<u>4044063</u>	August 1977	Ireland et al.	208/79 X
<u>4046829</u>	September 1977	Ireland et al.	208/88 X
<u>4046830</u>	September 1977	Kuo	208/120
<u>4052477</u>	October 1977	Ireland et al.	260/676R

ART-UNIT: 116

PRIMARY-EXAMINER: Gantz; Delbert E.

ASSISTANT-EXAMINER: Schmitkons; G. E.

ATTY-AGENT-FIRM: Huggett; Charles A. Farnsworth; Carl D.

ABSTRACT:

Fischer-Tropsch synthol naphtha is upgraded to high octane gasoline with minimum yield loss in a multistep process comprising fractionating the synthol naphtha to give a C_{sub}.5 + C_{sub}.6 fraction and C_{sub}.7_{sup}.+ fraction, processing the C_{sub}.5 + C_{sub}.6 fraction over a ZSM-5 catalyst under dense phase conditions, pretreating and reforming the C_{sub}.7_{sup}.+ fraction under conventional conditions, and blending the C_{sub}.5_{sup}.+ products from both the C_{sub}.5 + C_{sub}.6 and C_{sub}.7_{sup}.+ processing steps.

10 Claims, 3 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KMC
Draw Desc	Image									

[Generate Collection](#)

[Print](#)

Term	Documents
(10 NOT 11).USPT,PGPB,JPAB,EPAB,DWPI	9
(L10 NOT L11).USPT,PGPB,JPAB,EPAB,DWPI	9

Display Format:

[Previous Page](#) [Next Page](#)

End of Result Set

 Generate Collection

L12: Entry 9 of 9

File: USPT

Sep 5, 1978

DOCUMENT-IDENTIFIER: US 4111792 A

** See image for Certificate of Correction **

TITLE: Combination process for upgrading synthol naphtha fractions

Abstract Text (1):

Fischer-Tropsch synthol naptha is upgraded to high octane gasoline with minimum yield loss in a multistep process comprising fractionating the synthol naptha to give a C._{sub.5} + C._{sub.6} fraction and C._{sub.7.sup.+} fraction, processing the C._{sub.5} + C._{sub.6} fraction over a ZSM-5 catalyst under dense phase conditions, pretreating and reforming the C._{sub.7.sup.+} fraction under conventional conditions, and blending the C._{sub.5.sup.+} products from both the C._{sub.5} + C._{sub.6} and C._{sub.7.sup.+} processing steps.

Brief Summary Text (3):

This invention is concerned with a process for converting synthesis gas, i.e., mixtures of gaseous carbon oxides with hydrogen or hydrogen donors, to hydrocarbon mixtures and oxygenates. More particularly, this invention is concerned with upgrading a C._{sub.5.sup.+} fraction having an end-point of 340.degree. up to 400.degree. F obtained in a known Fischer-Tropsch synthesis process, so as to obtain a high yield of C._{sub.5.sup.+} gasoline of enhanced octane and a low-pour, high diesel index fuel oil.

Brief Summary Text (6):

It is considered desirable to effectively and more efficiently convert synthesis gas, and thereby coal and natural gas, to highly valued hydrocarbons such as motor gasoline with high octane number, petrochemical feedstocks, liquefiable petroleum fuel gas, and aromatic hydrocarbons. It is well known that synthesis gas will undergo conversion to form reduction products of carbon monoxides, such as hydrocarbons at from about 300.degree. to about 850.degree. F under from about one to one thousand atmospheres pressure, over a fairly wide variety of catalysts. The Fischer-Tropsch process, for example, which has been most extensively studied, produces a range of products including liquid hydrocarbons, a portion of which have been used as low octane gasoline. The types of catalysts that have been studied for this and related processes include those based on metals or oxides of iron, cobalt, nickel, ruthenium, thorium, rhodium and osmium.

Brief Summary Text (8):

Recently, a method for upgrading the C._{sub.5.sup.+} liquid product of a Fischer-Tropsch synthesis having an end point from about 340.degree.-400.degree. F has been discovered, which method comprises pretreating the C._{sub.5.sup.+} liquid product by hydrogenating it in the presence of a hydrogenation component (such as platinum or palladium) at conditions of temperature and pressure so as to selectively hydrogenate the diolefins contained in the C._{sub.5.sup.+} liquid product and thereafter contacting the hydrogenated product, at a temperature within the range of about 575.degree. to 850.degree. F and at a pressure within the range of about atmospheric to 700 psig, with a crystalline aluminosilicate having certain well-defined characteristics. This method is described in a copending United States patent application, Ser. No. 684,511, filed May 7, 1976, now U.S. Pat. No. 4,052,477. It should be noted that the elevated temperatures of the step following pretreatment are such that most or substantially all of the hydrogenated product from the pretreatment step will be in the gaseous phase during the second, aluminosilicate contacting step.

Brief Summary Text (9):

Still more recently, another method for upgrading the C._{sub.5+} liquid product of a Fischer-Tropsch synthesis having an end point from about 340.degree. to 400.degree. F has been discovered, which method comprises contacting the said liquid product in the absence of added hydrogen with a crystalline aluminosilicate, characterized by a pore dimension greater than about 5 Angstroms, a silica to alumina ratio of at least 12, and a constraint index within the range of 1 to 12 at dense phase process conditions of a temperature of about 400.degree. to 700.degree. F, a pressure of about 200 to 1000 psig, and a LHSV of about 0.1 to 2.0 and thereafter recovering a C._{sub.5+} gasoline product boiling up to about 400.degree. F having an enhanced octane value, a 400.degree.-650.degree. F fuel oil product, and a 650.degree. F..sup.+ product. This method is described in copending United States patent application Ser. No. 732,235 filed Oct. 14, 1976. It should be noted that the C._{sub.5+} liquid product is not fractionated prior to the aluminosilicate contacting step.

Brief Summary Text (11):

This invention is concerned with improving the product distribution and yield of products obtained by a Fischer-Tropsch synthesis gas conversion process. In a particular aspect, the present invention is concerned with upgrading the C._{sub.5}-400.degree. F liquid fraction of a synthesis gas conversion operation known in the industry as the Sasol Synthol process.

Brief Summary Text (12):

The Sasol process, located in South Africa, and built to convert an abundant supply of poor quality coal and products thereof to particularly hydrocarbons, oxygenates and chemical forming components was a pioneering venture. The process complex developed its enormous, expensive to operate and may be conveniently divided or separated into (1) a synthesis gas preparation complex from coal, (2) a Fischer-Tropsch type of synthesis gas conversion in both a fixed catalyst bed operation and a fluid catalyst bed operation, (3) a product recovery operation and (4) auxiliary plant and utility operations required in such a complex.

Brief Summary Text (13):

The extremely diverse nature of the products obtained in the combination operation of the Sasol process amplifies the complexity of the overall process complex, its product recovery arrangement and its operating economics. The Sasol synthesis operation is known to produce a wide spectrum of products including fuel gas, light olefins, LPG, gasoline, light and heavy fuel oils, waxy oils and oxygenates identified as alcohols, acetone, ketones and acids, particularly acetic and propionic acid. The C._{sub.2} and lower boiling components may be reformed to carbon monoxide and hydrogen or the C._{sub.2} formed hydrocarbons and methane may be combined and blended for use in a fuel gas pipeline system.

Brief Summary Text (14):

In the Sasol operation, the water soluble chemicals are recovered as by steam stripping distillation and separated into individual components with the formed organic acids remaining in the water phase separately treated. Propylene and butylene formed in the process are converted to gasoline boiling components as by polymerization in the presence of a phosphoric acid catalyst and by alkylation. Propane and butane on the other hand are used for LPG.

Brief Summary Text (15):

The present invention is concerned with improving a Fischer-Tropsch synthesis gas conversion operation and is particularly directed to improving the synthetic gasoline product selectivity and quality obtained by fractionating C._{sub.5}-400.degree. F material to give a C._{sub.5} + C._{sub.6} fraction and a C._{sub.7} + fraction and thereafter separately processing those fractions. It has been found that improved gasoline yield can be obtained by processing the C._{sub.5} + C._{sub.6} fraction over a ZSM-5 catalyst under dense phase conditions and pretreating and reforming the C._{sub.7}.sup.+ fraction under conventional conditions. The C._{sub.5}.sup.+ products from both processes are blended together, resulting in a gasoline yield which is greater than that obtained by reforming the entire C._{sub.5}.sup.+ naphtha to the same octane number and is also greater than that obtained by reforming the C._{sub.7}.sup.+ more severely to get the same pool octane when blended with the raw untreated C._{sub.5} + C._{sub.6} fraction.

Brief Summary Text (16):

Although combined oxygen in the charge is only partially removed by the present invention, complete oxygen removal is possible by a subsequent hydrotreatment of the

gasoline product over a hydrotreating catalyst at 50-300 psig, 500.degree.-600.degree. F, 0.2-10 LHSV, and 200-700 SCF H.sub.2 /bbl, with little or no octane loss.

Brief Summary Text (17):

The hydrotreating catalyst may be any of those known in the art, such as metals or compounds of subgroups V to VIII of the Periodic Table. A preferred catalyst is one containing a metal oxide or sulfide of Group VI (e.g., Mo) combined with a transition group metal oxide or sulfide (e.g., Co or Ni). Such catalysts may be used in undiluted form but normally are supported on an adsorbent carrier such as alumina, silica, zirconia, titania, and naturally occurring porous supports, e.g., activated high alumina ores such as bauxite or clays such as bentonite, etc. The preferred catalyst is Co/Mo/Alumina.

Drawing Description Text (2):

FIG. 1 is a condensed, schematic, block-flow arrangement of a known Fischer-Tropsch syngas conversion process directed to the conversion of coal to synthesis gas comprising carbon monoxide and hydrogen and the reduction of carbon monoxide by the Fischer-Tropsch process to form a product mixture comprising hydrocarbon and oxygenates and the recovery of these products for further use.

Drawing Description Text (3):

FIG. 2 is a plot of product yields and C.sub.5.sup.+ naphtha R.O.N. (R + O) versus dense phase processing temperature derived from an example of treating the C.sub.5 + C.sub.6 fraction of C.sub.5.sup.+ liquid product from a Fischer-Tropsch synthesis according to the method of this invention.

Drawing Description Text (4):

FIG. 3 is a yield-octane plot for low pressure reforming of pretreated C.sub.5.sup.+ and C.sub.7.sup.+ liquid products from a Fischer-Tropsch synthesis.

Detailed Description Text (2):

Referring now to FIG. 1, there is shown in block-flow arrangement a substantially reduced process flow arrangement of the Sasol syngas conversion process. A coal gasifier section 2 is provided to which pulverized coal is introduced by conduit 4, steam by conduit 6 and oxygen by conduit 8. The products of gasifier section 2 are then passed by conduit 10 to a gas scrubber section 12. In scrubber section 12, carbon monoxide and hydrogen-producing gases are separated from hydrogen sulfide which is removed by conduit 14, carbon dioxide removed by conduit 16, tars and phenols removed by conduit 18 and ammonia removed by conduit 20. The carbon monoxide-hydrogen producing gas is passed from section 12 by conduit 22 to a partial combustion zone 24 supplied with steam by conduit 26 and oxygen by conduit 28. Recycle C.sub.2 fuel gas product of the combination process after separation of carbon dioxide therefrom is recycled by conduit 30 to the partial combustion section 24. In the partial combustion operation 24, a suitable carbon monoxide-hydrogen rich synthesis gas of desired ratio is formed for use in a downstream Fischer-Tropsch synthesis gas conversion operation.

Detailed Description Text (3):

The Sasol process operates two versions of the Fischer-Tropsch process; one being a fixed catalyst bed operation and the other being a fluid catalyst bed operation. Each of these operations use iron catalyst prepared and presented to obtain desired catalyst composition and activity. The synthesis gas prepared as above briefly identified is passed by conduit 32 to the Fischer-Tropsch reaction section 36 in admixture with recycle gas introduced by conduit 34 at a temperature of about 160.degree. C and at an elevated pressure of about 365 psig. The temperature of the synthesis gas admixed with catalyst in the fluid operation rapidly rises by the heat liberated so that the Fischer-Tropsch and water gas shift reactions take place. The products of the Fischer-Tropsch synthesis reaction are conveyed by conduit 38 to a primary cooling section 40 wherein the temperature of the mixture is reduced to within the range of 280.degree. to about 400.degree. F. In a primary cooling section, a separation is made which permits the recovery of a slurry oil and catalyst stream by conduit 42, and a decant oil stream by conduit 44. In one typical operation, the decant oil stream will have an ASTM 95 percent boiling point of about 900.degree. F. A light oil stream oil stream boiling below about 560.degree. F and lower boiling components including oxygenates is passed by conduit 46 to a second or final cooling and separating section 48. In cooling section 48, a separation is made to recover a water phase comprising water-soluble oxygenates and chemicals withdrawn by conduit 50, a relatively light hydrocarbon phase boiling below about 560.degree. F withdrawn

by conduit 52 and a normally vaporous phase withdrawn by conduit 54. A portion of the vaporous phase comprising unreacted carbon monoxide and hydrogen is recycled by conduit 34 to conduit 32 charging syngas to the Fischer-Tropsch synthesis operation. In a typical operation, about one volume of fresh feed is used with two volumes of recycle gas. The hydrocarbons do not completely condense and an absorber system is used for their recovery. Methane and C._{sub.2} hydrocarbons are blended with other components in a pipeline system or they are passed to a gas reforming section for recycle as feed gas in the synthesis operation. The light hydrocarbon phase in conduit 52 is then passed through a water wash section 56 provided with wash water by conduit 58. In wash section 56, water-soluble materials comprising oxygenates are removed and withdrawn therefrom by conduit 60. The water phases in conduits 50 and 60 are combined and passed to a complicated and expensive-to-run chemicals recovery operation 62. The washed light hydrocarbon phase is removed by conduit 64 and passed to a clay treater 66 along with hydrocarbon fraction boiling below about 650.degree. F recovered from the decanted oil phase in conduit 44 and a heavy oil product fraction recovered as hereinafter described. The hydrocarbon phase thus recovered and passed to this clay treating section is preheated to an elevated temperature of above about 600.degree. F or higher before contacting the catalyst or clay in the treater. This clay treatment isomerizes hydrocarbons and particularly the alpha olefins in the product, thereby imparting a higher octane rating to these materials. The treatment also operates to convert harmful acids and other oxygenates retained in the hydrocarbon phase after the water wash. The clay treated hydrocarbon product is passed by conduit 68 to a hydrocarbon separation reaction 70. A portion of the hydrocarbon vapors in conduit 54 not directly recycled to the Fischer-Tropsch conversion operation by conduit 34 is also passed to the hydrocarbon separation reaction 70. In the hydrocarbon separation section 70, a separation is made to recover a fuel gas stream comprising C._{sub.2} hydrocarbons withdrawn by conduit 72. A portion of this material is passed through a CO._{sub.2} scrubber 74 before recycle by conduit 30 to the partial combustion zone 24. A portion of the fuel gas may be withdrawn by conduit 76. In separation section 70, a C._{sub.2} olefin-rich stream is recovered by conduit 78 for chemical processing as desired. A C._{sub.3} to C._{sub.4} hydrocarbon stream rich in olefins is withdrawn by conduit 80 and passed to catalytic polymerization in section 82. Polymerized material suitable for blending with gasoline product is withdrawn by conduit 84. A C._{sub.5}.sup.+ gasoline product fraction having an end point in the range of 340.degree. to 360.degree. up to 400.degree. F is recovered by conduit 86 and a light fuel oil product such as No. 2 fuel oil is withdrawn by conduit 90 for admixture with the decant oil fraction in conduit 44 as mentioned above. The blend of hydrocarbons product thus formed will boil in the range of about 400.degree. to about 1000.degree. F. This material blend is passed to a separator section 92 wherein a separation is made to recover a fraction boiling in the range of from about 400.degree. to 650.degree. F withdrawn by conduit 44 from a heavier higher boiling waxy oil withdrawn by conduit 96.

Detailed Description Text (4):

In this relatively complicated synthesis gas conversion operation and product recovery, it is not unusual to recover a product distribution comprising 2 percent ethylene, 8 percent LPG, 70 percent gasoline boiling material, 3 percent fuel oil, 3 percent waxy oil and about 14 percent of materials defined as oxygenates.

Detailed Description Text (5):

This Fischer-Tropsch synthesis operation above briefly defined and known in the industry as the Sasol Synthol process can be significantly improved following the concepts of this invention. It is the purpose of the invention to substantially upgrade the C._{sub.5} - 340.degree. to 400.degree. F gasoline fraction (i.e., the product from conduit 86 prior to blending via conduit 84) by first fractionating the C._{sub.5} - 340.degree. to 400.degree. F gasoline product from conduit 86 to separate a C._{sub.5} + C._{sub.6} fraction and a C._{sub.7}.sup.+ fraction and then separately processing these separated fractions.

Detailed Description Text (27):

Natural zeolites may sometimes be converted to this type zeolite by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination alone or in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite and clinoptilolite. The preferred crystalline aluminosilicates are ZSM-5, ZSM-11, ZSM-12 and ZSM-21, with ZSM-5 particularly preferred.

Detailed Description Text (36):

After pretreatment/reforming of the separated C._{sub.7}.sup.+ fraction by conventional

methods and dense phase processing of the separated C.sub.5 + C.sub.6 fraction, the C.sub.5.sup.+ products from both processes are blended together, yielding relatively high quantities of high-octane gasoline.

Detailed Description Text (39):

A C.sub.5 - 400.degree. F liquid fraction product of Fischer-Tropsch synthesis was distilled to separate a C.sub.5 + C.sub.6 fraction. The separated C.sub.5 + C.sub.6 fraction was passed over HZSM-5 extrudate at 700 psig, 1 LHSV, and temperatures of 300.degree. to 600.degree. F. Properties of the C.sub.5 + C.sub.6 charge are shown in Table I. The HZSM-5 extrudate contained 35 percent alumina binder, was sized to 30-60 mesh, and was charged to a 9/32 inch i.d. s.s. tubing reactor where it was pretreated with hydrogen at 900.degree. F for one hour. After catalyst pretreatment, the reactor was pressured to 700 psig with nitrogen against a grove loader, and then the C.sub.5 + C.sub.6 charge was pumped down-flow over the catalyst bed at reaction temperature. Yields and properties of products are listed in Table I and are plotted against temperature in FIG. 2.

Detailed Description Text (48):

Table IV lists the combined yields at 93 R + O pool octane. The C.sub.5.sup.+ yield from reforming the total C.sub.5.sup.+ charge to 93 R + O is 74 volume percent. Combining unprocessed C.sub.5 + C.sub.6 fraction (84 R + O) with the reformatre from C.sub.7.sup.+ charge at 97 R + O gives 77 volume percent 93 pool octane C.sub.5.sup.+ gasoline - a 3 volume percent yield gain over that obtained from reforming the C.sub.5.sup.+ charge to 93 (R + O) octane. An additional 1 volume percent increase is obtained by combining the dense phase processed C.sub.5 + C.sub.6 fraction (92 R + O) with reformatre from C.sub.7.sup.+ charge at 94 R + O according to the process of this invention. Furthermore, the yield advantage for the combination process will increase with higher pool octanes.

Detailed Description Paragraph Table (4):

Table I

Run Number 1 2 3 4 5 6 7 8

	Run Time,																	
Hrs.	24	221/2	17	5	16	5	61/2	51/2	Days on Stream	1.0	2.0	2.8	3.0	3.7	4.0	4.3	4.5	
LHSV Charge	1.3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	Temp., .degree. F, Average	452	501	401	350	551	450	600	301	
Maximum	455	507	402	352	558	452	604	305	Liquid Product Gravity, .degree. API	79.8	61.2	55.6	70.2	75.7	57.0	57.4	55.6	
.6697	.7343	.7563	.7015	.6829	.7507	.7491	.7563	.6803	Sim. Dist. 50% B.P., .degree. F	142	307	356	163	158	323	337	270	
Yields, Wt. %	C.sub.1	-C.sub.3	0.1	0.2	0.1	0.1	--	0.5	0.4	2.7	0.9	C.sub.4	's Total	6.1	2.9	2.8	4.5	
6.1	2.9	2.8	4.5	3.8	5.9	4.4	9.4	4.9	i-C.sub.4	--	0.1	0.5	0.1	--	2.1	1.6	4.9	
C.sub.4 =	5.2	1.5	0.6	3.6	3.2	1.7	1.2	0.8	3.9	n-C.sub.4	0.9	1.3	1.7	0.8	0.6	2.1	1.6	
3.7	0.8	C.sub.5	's Total	34.5	19.6	14.2	29.6	30.5	23.7	20.3	20.7	30.6	i-C.sub.5	0.9	2.0	3.2	1.3	
2.0	3.2	1.3	0.9	5.8	4.0	0.2	1.1	C.sub.5 =	29.9	11.0	3.2	23.8	25.9	9.7	9.0	5.6	25.9	
n-C.sub.5	3.7	6.6	8.0	4.5	3.7	8.2	7.3	6.9	3.6	C.sub.6	's Total	53.8	24.7	12.0	47.4	56.3	15.9	.sup.(2)
.sup.(2)	.sup.(3)	57.6	i-C.sub.6	1.9	3.9	3.9	3.0	3.1	6.2	2.0	C.sub.6 =	46.5	14.9	1.9	38.1	45.8	3.0	46.2
n-C.sub.6	4.8	5.5	5.5	5.6	6.1	6.2	8.6	Cycloparaffin	0.2	0.2	0.4	0.5	1.0	0.8	0.4	Benzene	0.4	0.2
0.2	0.2	0.4	0.5	1.0	0.8	0.4	0.4	0.2	0.3	0.2	0.3	0.2	0.4	C.sub.7.sup.+	5.5	52.6	60.7	
100.0	100.0	100.0	C.sub.5.sup.+	Naphtha	Wt. % of charge	93.8	79.9	57.6	95.4	96.2	53.4	Insufficient	94.2	Gravity, .degree. API	78.8	66.5	63.1	69.4
53.4	Gravity, Specific	.6728	.7146	.7271	0.7045	0.6849	.7086	Sample	0.6819	O.N., R + O	(MM)	84	88.3	83.9	92.0	91.5	83.3	400.degree. F.sup.+ Fuel Oil Wt. % of Charge
17.0	39.5	--	--	40.2	For	--	Gravity, .degree. API	--	43.9	43.8	--	--	39.7	--	Gravity, Specific	--	.8067	.8072
--	--	<-70	<-70	<-70	--	Aniline No., .degree. F	--	144.9	167.5	--	--	162.0	--	Diesel Index	--	64	73	--
Diesel Index	--	64	73	--	--	64	--											

.sup.(1)
Trace of aqueous layer in liquid product. .sup.(2) Total C.sub.6.sup.+ yield = 74.9 weight percent. .sup.(3) Total C.sub.6.sup.+ yield = 67.2 weight percent. At reaction temperatures of 450.degree. to 550.degree. F, products are formed with boiling points above 400.degree. F, very low pour points (<-70.degree. F) and high diesel indices (65-70) (See data for run numbers 1, 2, and 5 in Table I). The properties of this fraction are very similar to those obtained on the 400.degree. .sup.+ product when charging the whole C.sub.5.sup.- 400.degree. F synthol naphtha to dense phase processing.

Detailed Description Paragraph Table (7):

Table IV

Combined Yields at 93 Pool Octane (R+O) Reforming C.sub.7.sup.+ Reforming Blend with Blend with Dense C.sub.5.sup.+ Unprocessed C.sub.5 + C.sub.6.sup. (a) Phase Processed C.sub.5 + C.sub.6.sup. (b)

C.sub.5.sup.+ Yield, Vol. % 74.0 77.2 78.1 C.sub.5.sup.+ O.N., R+O 93.0 93.0 93.3
Yields, Wt. % H.sub.2 1.4 1.3 1.2 C.sub.1 1.2 1.1 0.9 C.sub.2 2.8 2.6 2.3 C.sub.3 7.3 6.4 6.0 C.sub.4 9.6 8.6 7.9 C.sub.5.sup.+ 77.6 80.0 81.7 100.0 100.0 100.0

.sup. (a)
C.sub.7.sup.+ reformed to 97 R+O, raw C.sub.5 + C.sub.6 84 R+O, linear blending
.sup. (b) C.sub.7.sup.+ reformed to 94 R+O, dense phase processed C.sub.5 C.sub.6 92
R+O, linear blending

CLAIMS:

1. A method for upgrading the C.sub.5 + liquid product of a Fischer-Tropsch synthesis having an end-point from about 340.degree. to 400.degree. F which comprises:

- (a) fractionating said liquid product to separate a C.sub.5 + C.sub.6 fraction and a C.sub.7 + fraction;
- (b) reforming the C.sub.7 + fraction to produce a C.sub.5 + reformate;
- (c) containing the C.sub.5 + C.sub.6 fraction in the absence of added hydrogen with a crystalline aluminosilicate characterized by a pore dimension greater than about 5 Angstroms, a silica to alumina ratio of at least 12, a constraint index within the range of 1 to 12 at dense phase process conditions of a temperature of about 325.degree. to 500.degree. F, a pressure of about 200 to 1000 psig, and a LHSV of about 0.1 to 5.0; and
- (d) recovering a C.sub.5 gasoline product boiling up to about 400.degree. F having an enhanced octane value from the dense phase processed C.sub.5 + C.sub.6 fraction; and
- (e) blending said C.sub.5 + reformate with said C.sub.5 gasoline product.

3. A method for upgrading the C.sub.5 + liquid product of a Fischer-Tropsch synthesis having an end-point from about 340.degree. to 400.degree. F which comprises:

- (a) fractionating the liquid product to separate a C.sub.5 + C.sub.6 fraction and a C.sub.7 + fraction;
- (b) pretreating the C.sub.7 + fraction by mild hydrogenation over a Co/Mo/Alumina catalyst;
- (c) catalytically reforming the C.sub.7 + fraction to produce a C.sub.5 + reformate;
- (d) contacting the C.sub.5 + C.sub.6 fraction in the absence of added hydrogen with a crystalline aluminosilicate selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-35, and ZSM-38 at dense phase process conditions of a temperature of about 325.degree. to 500.degree. F, a pressure of 600 to 700 psig, and a LHSV of about 0.1 to 5.0; and
- (e) recovering a C.sub.5 gasoline product boiling up to about 400.degree. F having an enhanced octane value from the dense phase processed C.sub.5 + C.sub.6 fraction; and
- (f) blending said C.sub.5 + reformate with said C.sub.5 gasoline product.

4. The process of claim 3 wherein the C.sub.5 + gasoline product recovered from the dense phase processed C.sub.5 + C.sub.6 fraction is hydrotreated prior to blending with the C.sub.5 + reformate to produce a deoxygenated, gasoline boiling product of enhanced octane value.

L14: Entry 5 of 11

File: USPT

Aug 14, 2001

DOCUMENT-IDENTIFIER: US 6274029 B1

TITLE: Synthetic diesel fuel and process for its production

Abstract Text (1):

Diesel fuels or blending stocks having excellent lubricity, oxidative stability and high cetane number are produced from non-shifting Fischer-Tropsch processes by separating the Fischer-Tropsch product into a lighter and heavier fractions, e.g., at about 700.degree. F., subjecting the 700.degree. F.+fraction to hydro-treating, and combining the 700.degree. F.+portion of the hydrotreated product with the lighter fraction that has not been hydrotreated.

Brief Summary Text (2):

This invention relates to a distillate material having a high cetane number and useful as a diesel fuel or as a blending stock therefor, as well as the process for preparing the distillate. More particularly, this invention relates to a process for preparing distillate from a Fischer-Tropsch wax.

Brief Summary Text (4):

Clean distillates that contain no or nil sulfur, nitrogen, or aromatics, are, or will likely be in great demand as diesel fuel or in blending diesel fuel. Clean distillates having relatively high cetane number are particularly valuable. Typical petroleum derived distillates are not clean, in that they typically contain significant amounts of sulfur, nitrogen, and aromatics, and they have relatively low cetane numbers. Clean distillates can be produced from petroleum based distillates through severe hydrotreating at great expense. Such severe hydrotreating imparts relatively little improvement in cetane number and also adversely impacts the fuel's lubricity. Fuel lubricity, required for the efficient operation of fuel delivery system, can be improved by the use of costly additive packages. The production of clean, high cetane number distillates from Fischer-Tropsch waxes has been discussed in the open literature, but the processes disclosed for preparing such distillates also leave the distillate lacking in one or more important properties, e.g., lubricity. The Fischer-Tropsch distillates disclosed, therefore, require blending with other less desirable stocks or the use of costly additives. These earlier schemes disclose hydrotreating the total Fischer-Tropsch product, including the entire 700.degree. F.- fraction. This hydro-treating results in the elimination of oxygenates from the distillate.

Brief Summary Text (5):

By virtue of this present invention small amounts of oxygenates are retained, the resulting product having both very high cetane number and high lubricity. This product is therefore useful as a diesel fuel as such, or as a blending stock for preparing diesel fuels from other lower grade material.

Brief Summary Text (7):

In accordance with this invention, a clean distillate useful as a fuel heavier than gasoline, e.g., useful as a diesel fuel or as a diesel fuel blend stock and having a cetane number of at least about 60, preferably at least about 70, more preferably at least about 74, is produced, preferably from a Fischer-Tropsch wax and preferably derived from a cobalt or ruthenium Fischer-Tropsch catalyst, by separating the waxy product into a heavier fraction and a lighter fraction. The nominal separation is at about 700.degree. F., and the heavier fraction contains primarily 700.degree. F.+, and the lighter fraction contains primarily 700.degree. F.--.

Detailed Description Text (2):

A more detailed description of this invention may be had by referring to the

drawing. Synthesis gas, hydrogen and carbon monoxide, in an appropriate ratio, contained in line 1 is fed to a Fischer-Tropsch reactor 2, preferably a slurry reactor and product is recovered in lines 3 and 4, 700.degree. F.+ and 700.degree. F.- respectively. The lighter fraction goes through hot separator 6 and a 500-700.degree. F. fraction is recovered, in line 8, while a 500.degree. F.- fraction is recovered in line 7. The 500.degree. F.- material goes through cold separator 9 from which C.sub.4 -gases are recovered in line 10. A C.sub.5 -500.degree. F. fraction is recovered in line 11 and is combined with the 500-700.degree. F. fraction in line 8. At least a portion and preferably most, more preferably essentially all of this C.sub.5 -700 fraction is blended with the hydroisomerized product in line 12.

Detailed Description Text (12):

The iso paraffins are preferably mono methyl branched, and since the process utilizes Fischer-Tropsch wax, the product contains nil cyclic paraffins, e.g., no cyclohexane.

Detailed Description Text (13):

The oxygenates are contained essentially, e.g., >95% of the oxygenates, in the lighter fraction, e.g., the 700.degree. F.- fraction. Further, the olefin concentration of the lighter fraction is sufficiently low as to make olefin recovery unnecessary; and further treatment of the fraction for olefins is avoided.

Detailed Description Text (14):

The preferred Fischer-Tropsch process is one that utilizes a non-shifting (that is, no water gas shift capability) catalyst, such as cobalt or ruthenium or mixtures thereof, preferably cobalt, and preferably a promoted cobalt, the promoter being zirconium or rhenium, preferably rhenium. Such catalysts are well known and a preferred catalyst is described in U.S. Pat. No. 4,568,663 as well as European Patent 0 266 898. The hydrogen:CO ratio in the process is at least about 1.7, preferably at least about 1.75, more preferably 1.75 to 2.5.

Detailed Description Text (15):

The products of the Fischer-Tropsch process are primarily paraffinic hydrocarbons. Ruthenium produces paraffins primarily boiling in the distillate range, i.e., C.sub.10 -C.sub.20 ; while cobalt catalysts generally produce more of heavier hydrocarbons, e.g., C.sub.20 +, and cobalt is a preferred Fischer-Tropsch catalytic metal.

Detailed Description Text (18):

By virtue of using the Fischer-Tropsch process, the recovered distillate has nil sulfur and nitrogen. These hereto-atom compounds are poisons for Fischer-Tropsch catalysts and are removed from the methane containing natural gas that is a convenient feed for the Fischer-Tropsch process. (Sulfur and nitrogen containing compounds are, in any event, in exceedingly low concentrations in natural gas.) Further, the process does not make aromatics, or as usually operated, virtually no aromatics are produced. Some olefins are produced since one of the proposed pathways for the production of paraffins is through an olefinic intermediate. Nevertheless, olefin concentration is usually quite low.

Detailed Description Text (19):

Oxygenated compounds including alcohols and some acids are produced during Fischer-Tropsch processing, but in at least one well known process, oxygenates and unsaturates are completely eliminated from the product by hydrotreating. See, for example, The Shell Middle Distillate Process, Eiler, J.; Posthuma, S.A.; Sie, S.T., Catalysis Letters, 1990, wt, 253-270.

Detailed Description Text (20):

We have found, however, that small amounts of oxygenates, preferably alcohols, usually concentrated in the 700.degree. F.- fraction and preferably in the 500-700.degree. F. fraction, more preferably in the 600-700.degree. F. fraction, provide exceptional lubricity for diesel fuels. For example, as illustrations will show, a highly paraffinic diesel fuel with small amounts of oxygenates has excellent lubricity as shown by the BOCLE test (ball on cylinder lubricity evaluator). However, when the oxygenates were removed, for example, by extraction, absorption over molecular sieves, hydroprocessing, etc., to a level of less than 10 ppm wt% oxygen (water free basis) in the fraction being tested, the lubricity was quite poor.

Detailed Description Text (21):

By virtue of the processing scheme disclosed in this invention the lighter, 700.degree. F.- fraction is not subjected to any hydrotreating. In the absence of hydrotreating of the lighter fraction, the small amount of oxygenates, primarily linear alcohols, in this fraction are preserved, while oxygenates in the heavier fraction are eliminated during the hydroisomerization step. Hydroisomerization also serves to increase the amount of iso paraffins in the distillate fuel and helps the fuel to meet pour point and cloud point specifications, although additives may be employed for these purposes.

Detailed Description Text (23):

Preferred oxygen compounds, primarily alcohols, have a relatively long chain, i.e., C.sub.12 +, more preferably C.sub.12 +C.sub.24 primary linear alcohols.

Detailed Description Text (24):

While acids are oxygen containing compounds, acids are corrosive and are produced in quite small amounts during Fischer-Tropsch processing at non-shift conditions. Acids are also di-oxygenates as opposed to the preferred mono-oxygenates illustrated by the linear alcohols. Thus, di or poly-oxygenates are usually undetectable by infrared measurements and are, e.g., less than about 15 wppm oxygen as oxygen.

Detailed Description Text (25):

Non-shifting Fischer-Tropsch reactions are well known to those skilled in the art and may be characterized by conditions that minimize the formations of CO.sub.2 byproducts. These conditions can be achieved by a variety of methods, including one or more of the following: operating at relatively low CO partial pressures, that is, operating at hydrogen to CO ratios of at least about 1.7/1, preferably about 1.7/1 to about 2.5/1, more preferably at least about 1.9/1, and in the range 1.9/1 to about 2.3/1, all with an alpha of at least about 0.88, preferably at least about 0.91; temperatures of about 175-225.degree. C., preferably 180-210.degree. C.; using catalysts comprising cobalt or ruthenium as the primary Fischer-Tropsch catalysts agent.

Detailed Description Text (26):

The amount of oxygenates present, as oxygen on a water free basis is relatively small to achieve the desired lubricity, i.e., at least about 0.001 wt% oxygen (water free basis), preferably 0.001-0.3 wt % oxygen (water free basis), more preferably 0.0025-0.3 wt % oxygen (water free basis).

Detailed Description Text (28):

Hydrogen and carbon monoxide synthesis gas (H.sub.2 :CO 2.11-2.16) were converted to heavy paraffins in a slurry Fischer-Tropsch reactor. The catalyst utilized for the Fischer-Tropsch reaction was a titania supported cobalt/rhenium catalyst previously described in US Pat. No. 4,568,663. The reaction conditions were 422-428.degree. F., 287-289 psig, and a linear velocity of 12 to 17.5 cm/sec. The alpha of the Fischer-Tropsch synthesis step was 0.92. The paraffinic Fischer-Tropsch product was then isolated in three nominally different boiling streams, separated utilizing a rough flash. The three approximate boiling fractions were: 1) the C.sub.5 +500.degree. F. boiling fraction, designated below as F-T Cold Separator Liquids; 2) The 500-700.degree. F. boiling fraction designated below as F-T Hot Separator Liquids; and 3) the 700.degree. F.+ boiling fraction designated below as F-T Reactor Wax.

Detailed Description Text (30):

Seventy wt % of a Hydroisomerized F-T Reactor Wax, 16.8 wt % Hydrotreated F-T Cold Separator Liquids and 13.2 wt% Hydrotreated F-T Hot Separator Liquids were combined and rigorously mixed. Diesel Fuel A was the 260-700.degree. F. boiling fraction of this blend, as isolated by distillation, and was prepared as follows: The hydroisomerized F-T Reactor Wax was prepared in flow through, fixed bed unit using a cobalt and molybdenum promoted amorphous silica-alumina catalyst, as described in U.S. Pat. No. 5,292,989 and U.S. Pat. No. 5,378,348. Hydroisomerization conditions were 708.degree. F., 750 psig H.sub.2, 2500 SCF/B H.sub.2, and a liquid hourly space velocity (LHSV) of 0.7-0.8. Hydroisomerization was conducted with recycle of unreacted 700.degree. F.+ reactor wax. The Combined Feed Ratio, (Fresh Feed+Recycle Feed)/Fresh Feed equaled 1.5. Hydrotreated F-T Cold and Hot Separator Liquid were prepared using a flow through fixed bed reactor and commercial massive nickel catalyst. Hydrotreating conditions were 450.degree. F., 430 psig H.sub.2, 1000 SCF/B H.sub.2, and 3.0 LHSV. Fuel A is representative of a typical completely hydrotreated cobalt derived Fischer-Tropsch diesel fuel, well known in the art.

Detailed Description Text (36):

100.81 grams of Diesel Fuel B was contacted with 33.11 grams of Grace Silico-aluminate zeolite: 13X Grade 544, 8-12 mesh beads. Diesel Fuel E is the filtrated liquid resulting from this treatment. This treatment effectively removes alcohols and other oxygenates from the fuel.

Detailed Description Text (38):

Diesel Fuel F is a hydrotreated petroleum stream composed of approximately 40% cat distillate and 60% virgin distillate. It was subsequently hydrotreated in a commercial hydrotreater. The petroleum fraction has a boiling range of 250-800.degree. F., contains 663 ppm sulfur (x-ray), and 40% FIA aromatics. Diesel Fuel F represents a petroleum base case for this invention.

Detailed Description Text (40):

Diesel Fuel G was prepared by combining equal amounts of Diesel Fuel B with a Diesel Fuel F. Diesel Fuel G should contain 600 ppm total oxygen (neutron activation), 80 ppm 500+.degree. F. boiling primary alcohols the (GC/MS), and signal for primary alcohols indicates 320 ppm total oxygen as primary alcohols (.sup.1 H NMR; 250-700.degree. F.). Diesel Fuel G represents an additional example for this invention where both HCS and petroleum distillates are used to comprise the diesel fuel.

Detailed Description Text (42):

Oxygenate, dioxygenate, and alcohol composition of Diesel Fuels A, B, and E were measured using Proton Nuclear Magnetic Resonance (.sup.1 H-NMR), Infrared Spectroscopy (IR), and Gas Chromatography/Mass Spectrometry (GC/MS). .sup.1 H-NMR experiments were done using a Brucker MSL-500 Spectrometer. Quantitative data were obtained by measuring the samples, dissolved in CDCl₃, at ambient temperature, using a frequency of 500.13 MHz, pulse width of 2.9 .mu.s (45 degree tip angle), delay of 60 s, and 64 scans. Tetramethylsilane was used as an internal reference in each case and dioxane was used as an internal standard. Levels of primary alcohols, secondary alcohols, esters and acids were estimated directly by comparing integrals for peaks at 3.6 (2H), 3.4 (1H), 4.1 (2H) and 2.4 (2H) ppm respectively, with that of the internal standard. IR Spectroscopy was done using a Nicolet 800 spectro-meter. Samples were prepared by placing them in a KBr fixed path length cell (nominally 1.0 mm) and acquisition was done by adding 4096 scans a 0.3 cm.sup.-1 resolution. Levels of dioxygenates, such as carboxylic acids and esters, were measured using the absorbance at 1720 and 1738 cm.sup.-1, respectively. GC/MS were performed using either a Hewlett-Packard 5980/Hewlett-Packard 5970B Mass Selective Detector Combination (MSD) or Kratos Model MS-890 GC/MS. Selected ion monitoring of m/z 31 (CH₃O⁺) was used to quantify the primary alcohols. An external standard was made by weighing C₂-C₁₄, C₁₆ and C₁₈ primary alcohols into a mixture of C₈-C₁₆ normal paraffins. Olefins were determined using Bromine Index, as described in ASTM D 2710. Results from these analyses are presented in Table 1. Diesel Fuel B which contains the unhydrotreated hot and cold separator liquids contains a significant amount of oxygenates as linear, primary alcohols. A significant fraction of these are the important C₁₂-C₁₈ primary alcohols. It is these alcohols that impart superior performance in diesel lubricity. Hydrotreating (Diesel Fuel A) is extremely effective at removing essentially all of the oxygenates and olefins. Mole sieve treatment (Diesel Fuel E) also is effective at removing the alcohol contaminants without the use of process hydrogen. None of these fuels contain significant levels of dioxygenates, such as carboxylic acids or esters. A sample IR spectrum for Diesel Fuel B is shown in FIG. 2.

Detailed Description Text (45):

The completely hydrotreated Diesel Fuel A, exhibits very low lubricity typical of an all paraffin diesel fuel. Diesel Fuel B, which contains a high level of oxygenates as linear, C₅-C₂₄ primary alcohols, exhibits significantly superior lubricity properties. Diesel Fuel E was prepared by separating the oxygenates away from Diesel Fuel B through adsorption by 13X molecular sieves. Diesel Fuel E exhibits very poor lubricity indicating the linear C₅-C₂₄ primary alcohols are responsible for the high lubricity of Diesel Fuel B. Diesel Fuels C and D represent the 250-500.degree. F. and the 500-700.degree. F. boiling fractions of Diesel Fuel B, respectively. Diesel Fuel C contains the linear C₅-C₁₁ primary alcohols that boil below 500.degree. F., and Diesel Fuel D contains the C₁₂-C₂₄ primary alcohols that boil between 500-700.degree. F. Diesel Fuel D exhibits superior lubricity properties compared to Diesel Fuel C, and is in fact

superior in performance to Diesel Fuel B from which it is derived. This clearly indicates that the C.sub.12 -C.sub.24 primary alcohols that boil between 500-700.degree. F. are important to producing a high lubricity saturated diesel fuel. Diesel Fuel F is representative of petroleum derived low sulfur diesel fuel, and although it exhibits reasonably high lubricity properties it is not as high as the highly paraffinic Diesel Fuel B. Diesel Fuel G is the 1:1 blend of Diesel Fuel B and Diesel Fuel F and it exhibits improved lubricity performance compared to Diesel F. This indicates that the highly paraffinic Diesel Fuel B is not only a superior neat fuel composition, but also an outstanding diesel blending component capable of improving the properties of petroleum derived low sulfur diesel fuels.

Detailed Description Paragraph Table (3):

paraffins at least 95 wt %, preferably at least 96 wt %, more preferably at least 97 wt %, still more preferably at least 98 wt %, and most preferably at least 99 wt %; iso/normal ratio about 0.3 to 3.0, preferably 0.7-2.0; sulfur .ltoreq.50 ppm (wt), preferably nil; nitrogen .ltoreq.50 ppm (wt), preferably .ltoreq.20 ppm, more preferably nil; unsaturates .ltoreq.2 wt %; (olefins and aromatics) oxygenates about 0.001 to less than 0.3 wt % oxygen water-free basis

Detailed Description Paragraph Table (4):

TABLE 1 Oxygenate and dioxygenate (carboxylic acids, esters) composition of All Hydrotreated Diesel Fuel (Diesel Fuel A), Partially Hydrotreated Diesel Fuel (Diesel Fuel B), and the Mole Sieve Treated, Partially Hydrotreated Diesel Fuel (Diesel Fuel E). Diesel Diesel Diesel Fuel A Fuel B Fuel E wppm Oxygen in dioxygenates, None None None (carboxylic acids, esters) - (IR) Detected Detected Detected wppm Oxygen in C.sub.5 -C.sub.18 None 640 ppm None primary alcohols - (.sup.1 H NMR) Detected Detected wppm Oxygen in C.sub.5 -C.sub.18 5.3 824 None primary alcohols - (GC/MS) Detected wppm Oxygen in C.sub.12 -C.sub.18 3.3 195 ppm None primary alcohols - (GC/MS) Detected Total Olefins - mmol/g (Bromine 0.004 0.78 -- Index, ASTM D 2710)

Other Reference Publication (4):

Norton et al, "Emissions from Trucks using Fischer-Tropsch Diesel Fuel", SAE No. 982526, pp. 1-10 (1998).

Other Reference Publication (5):

Booth et al (Shell) "Severe hydrotreating of diesel can cause fuel-injector pump failure", PennWell Publishing Company, Oil & Gas Journal (Aug. 16, 1993).

Other Reference Publication (9):

Erwin et al., "The Standing of Fischer-Tropsch Diesel in an Assay of Fuel Performance and Emissons", Southwest Research Institute, Contract No. NREL SUB YZ-2-113215-1 (Oct. 26, 1993).

Other Reference Publication (15):

T. L. Ullman, "Effects of Cetane Number, Cetane Improver, Aromatics, and Oxygenates on 1994 Heavy-Duty Diesel Engine Emission", SAE Paper 841020.

Other Reference Publication (16):

K. B. Spreen, "Effects of Cetane Number, Aromatics, and Oxygenates on Emissions From a 1994 Heavy-Duty Diesel Engine With Exhaust Catalyst", SAE Paper 950250.

Other Reference Publication (37):

Shah et al, USDOE/USDOC NTIS, UOP, Inc., Fischer-Tropsch Wax Characterization and Upgrading--Final Report, DE 88-014638, Jun. 1988 ("UOP Report").

CLAIMS:

1. A material useful as a fuel heavier than gasoline or as a blending component for a distillate fuel comprising: a 250-700.degree. F. fraction derived from a non-shifting Fischer-Tropsch catalyst process and containing

at least 95 wt % paraffins with an iso to normal ratio of about 0.3 to 3.0,

<50 ppm (wt) of sulfur and nitrogen

less than about 2 wt % unsaturates, and

about 0.001 to less than 0.3 wt % oxygen.

2. The material of claim 1 wherein the oxygen is present primarily as linear alcohols.

3. The material of claim 2 wherein the linear alcohols are C._{sub}.12 +.

7. wt A blended fuel, useful as a diesel fuel, comprising:

(a) a 250-700.degree. F. distillate fraction derived from the Fischer-Tropsch process which contains;

at least 95 wt % paraffins with an iso to normal ratio of about 0.3 to 3.0,

<50 ppm (wt) each of sulfur and nitrogen,

less than about 2 wt % unsaturates

about 0.001 to less than 0.3 wt% linear oxygenate, as oxygen on a water free basis, blended with

(b) a petroleum derived hydrocarbon fraction, wherein the Fischer-Tropsch fraction comprises at least 10% of the blended fuel.

8. A blend according to claim 7 wherein said Fischer-Tropsch process is a non-shifting Fischer-Tropsch catalyst process.

9. A blend according to claim 6 wherein said Fischer-Tropsch catalyst comprises cobalt.